A MODEL FOR LIQUID PHASE METHANOL SYNTHESIS PROCESS IN A COCURRENT FLOW ENTRAINED REACTOR

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ABSTRACT

Experimental studies on the liquid phase synthesis of methanol were performed in an entrained reactor. In this three-phase process, syngas reacts in the presence of the catalyst-oil slurry, to form the product methanol. The effect of various operating conditions which included reactor temperature, pressure, flow rates of slurry and syngas, slurry holdup tank pressure, syngas composition and catalyst loadings, on the reactor productivity were studied. An overall experimental reaction rate model to predict the productivity of methanol using the operating conditions as the variables was developed, and the results were compared with the experimental data.

A computer model was also developed that predicts the reactivity of all species involved in the methanol synthesis process in an entrained reactor, from inlet conditions. This model incorporates the kinetic rate expression and the gas-liquid mass transfer correlation that was developed for the methanol synthesis process in a liquid entrained reactor. The rate of production of methanol predicted by this computer model agreed well with the experimental results. The overall experimental reaction rate model and the computer model assists in the development, scale-up and commercialization of the liquid phase methanol synthesis process in an entrained reactor.

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SIGNIFICANCE OF THE LIQUID PHASE METHANOL SYNTHESIS PROCESS

The liquid-phase methanol synthesis (LPMeOH) process that was developed by Chem Systems, Inc. in 1975 (Sherwin and Blum, 1979), was a three phase process that provided improved reactor stability and the compatibility of using a synthesis gas mixture with a higher CO content than H_2. However this process is not limited to CO-rich syngas only. The advantages of such a process in terms of reactant gas compositions include the use of coal derived feedstocks, and as a result, the process can be additionally significant in the production of clean liquid fuels (Lee, 1990).

The commercial reactor proposed for the LPMeOH process is an entrained reactor. In an entrained reactor, the catalyst particles in powder form are uniformly suspended in the liquid (oil) and this catalyst-oil slurry is continuously recirculated by a pump through a tubular reactor. Contact with the syngas is made by feeding the gas cocurrently with the upward flow of slurry (Vijayaraghavan and Lee, 1992). The inert liquid provides a much larger thermal mass than the vapor medium, thus facilitating the easier control of temperature by absorbing the exothermic heat generated during the methanol reaction.

The objective of this study is to develop an overall experimental reaction rate model to predict the production of methanol from operating conditions, and to develop a computer model to predict the reactivity of all species involved in the methanol synthesis process in a liquid entrained reactor, from inlet conditions. Such information is essential for the design, development and scale-up of the methanol synthesis process in a liquid entrained reactor.

MINI-PILOT PLANT ENTRAINED SLURRY REACTOR SYSTEM

A laboratory scale, continuous, mini-pilot plant was designed and built to carry out methanol synthesis research in a liquid entrained reactor (Vijayaraghavan, 1994). The details of the entrained reactor system and its peripherals is shown in Figure 1. The entrained reactor is a 76.2 cm. long stainless steel tube. Its outer diameter is 1.31 cm. The

feed gas and the catalyst-oil slurry are introduced cocurrently from the bottom of the reactor. This provides effective dispersion of gas bubbles and along with the high flow rate of slurry, ensures a good suspension of solid particles in liquid. The reactor is equipped with an external heating device, capable of raising the temperature of the fluids in the reactor to the desired operating temperature.

Syngas is passed to the reactor at a desired flow rate by a mass flow controller. A pneumatically operated air-to-close back pressure control valve with positioner, connected to a pressure controller, maintains the entrained reactor at the desired pressure. The slurry is recirculated in the entrained reactor by a specially designed plunger type reciprocating slurry pump, which is capable of handling slurries containing as high as 40 wt.% of metallic catalyst solids. The entrained reactor system is provided with a slurry holdup vessel that is thoroughly agitated by a Magnedrive impeller, to prevent the catalyst settling and agglomeration. The unreacted gases and the product vapors from the slurry holdup vessel flow to the condenser. A sample bottle is installed at the exit of the condenser. The oil free gas flows to the lower chamber of a back pressure regulator, which maintains the slurry holdup tank pressure at a lower pressure than the entrained reactor, to facilitate product flashing and thereby separating the product vapors from the catalyst-slurry system. The flow rate of the vent gas is measured using a wet test meter. The on-line analyses of the feed and product gases and liquid product are carried out using a gas chromatograph coupled to an integrator.

EXPERIMENTAL DESIGN AND PROCEDURE

The syngas blending and compression procedure and the catalyst activation procedure developed for low (< 25 wt. %) and high (> 25 wt. %) concentration of catalyst in slurry are published elsewhere (Sawant *et al.*, 1987; Vijayaraghavan, 1994). A FORTRAN program that was developed to compute the material balance of experiments across the reactor system is given elsewhere (Lee, 1990; Parameswaran, 1987).

In order to develop an overall reaction rate model and a computer model to predict the reactivity of all species involved in the methanol synthesis process in a liquid entrained reactor, a statistical design of experiments was established and performed. From initial studies, it was found that the reactor temperature, pressure, syngas and slurry flow rates, and slurry hold-up tank pressure, are the important variables. A fractional factorial (2^{5-2}) design was used and is explained elsewhere (Vijayaraghavan, 1994). The high and low levels for each variable were chosen so that commercially interesting conditions would lie in the middle of the design. The levels of the variables are shown in Table I. These experiments were repeated for three different catalyst loadings by weight (10 %, 25 %, and 35 %) in slurry, to cover the kinetic and mass transfer controlling regimes.

ANALYSIS OF EXPERIMENTAL DATA

Experiments were performed according to the design mentioned earlier and the data obtained for 10%, 25% and 35% concentration by weight of catalyst in slurry were analyzed to develop an overall reaction rate expression model and a computer model that would predict the production of methanol in an entrained reactor, for any given operating condition. The data points cover 2 levels of reactor temperature, reactor pressure, syngas flow rate, slurry holdup tank pressure, slurry flow rate, syngas composition, and 3 levels of catalyst concentration by weight in slurry.

Overall Rate Expression for LPMeOH Process in an Entrained Reactor

The development of an overall rate model is essential to predict the production of methanol in an entrained reactor, for any given operating condition. The 6 variables used for analyzing the data included reactor temperature, pressure, syngas flow rate, slurry holdup tank pressure, slurry flow rate, and catalyst concentration by weight in slurry. The overall rate expression for methanol productivity was developed using data described in detail elsewhere (Vijayaraghavan, 1994). The 6 variables were correlated using a SAS Program (PROC GLM) featuring a regression-correlation method that uses the principle of least squares to fit general linear models and generates the estimates of the unknowns.

The overall reaction rate expression for methanol productivity in an entrained reactor for the available data, can be best represented by the following statistical correlation model:

$$R_{MeOH} = 0.0027 \times T - 0.039 \times P - 24.75 \times F_g + 249.30 \times C + 7.6 \times 10^{-5} \times T \times P + 0.044 \times T \times F_g - 0.445 \times T \times C + 0.0026 \times P \times F_g + 9.7 \times 10^{-6} \times P \times P_H - 0.03 \times P \times C - 0.003 \times F_g \times P_H + 0.025 \times F_g \times F_s + 0.405 \times F_g \times C + 5.7 \times 10^{-4} \times P_H \times C \quad \ldots (1)$$

where R_{MeOH}, T, P, F_g, P_H, F_s, and C represent the rate of methanol production (mol/kg.cat-h), reactor temperature (K), reactor pressure (psi), syngas flow rate (SLPM),

slurry holdup tank pressure (psi), flow rate of slurry (l/h), and catalyst concentration in slurry (weight fraction), respectively.

It is seen from Figure 2 that the rate of methanol production predicted by Equation (1), match very well with the experimental rate data. It is observed that the average error between the experimental and the predicted rate values is 9.5%. Considering the range of practical experimental operating conditions and the inherent experimental error, the average deviation of the model seems quite good.

The overall rate expression shown in Equation (1) can help to predict the methanol production for any given operating condition, and would be extremely useful for process design, development and scale-up computations.

Computer Modeling of the Liquid Entrained Reactor

Modeling of the liquid entrained reactor was carried out to predict the reactor productivity from inlet conditions. This computer program can accurately predict the multicomponent phase equilibria, ultimate chemical equilibria, and compositions of all reactant and product species exiting in the entrained reactor. Intrinsic reaction rate expressions and overall rate expressions based on the gas-liquid mass transfer correlation were developed earlier (Vijayaraghavan, 1994).

For CO-rich syngas, the intrinsic reaction rate expression is:

$$R_{MeOH} = 0.75 \times 10^{10} \, Exp(-20500/RT) \, (C_{H2} - C_{H2}^{eq}) \qquad \ldots (2)$$

For H_2-rich syngas, the intrinsic reaction rate expression is:

$$R_{MeOH} = 0.41 \times 10^{10} \, Exp(-20500/RT) \, (C_{H2} - C_{H2}^{eq}) \qquad \ldots (3)$$

The overall reaction rate expression in terms of gas-liquid mass transfer coefficient is (Lee, 1990):

$$R_{MeOH} = (V_{oil}/W) \, (M^{-1}) \, (C_{H2} - C_{H2}^{eq}) \qquad \ldots (4)$$

$$M = (V_{oil}/W) \, (1/k_r) + (1/K_{Li}a_B) \qquad \ldots (5)$$

In Equations (2), (3), (4), and (5), R, V_{oil}, W, $K_{Li}a_B$, k_r, C_{H2}, and C_{H2}^{eq} represent the universal gas constant (l-atm./mol-K), volume of oil at operating conditions (l), mass of catalyst in slurry (kg), overall gas-liquid mass transfer coefficient (1/h), intrinsic reaction rate constant represented by Equations (2) and (3), and the physical and chemical equilibrium concentrations of hydrogen in oil (mol/l), respectively.

The overall gas-liquid mass transfer coefficient was best represented by the following correlation:

$$N_{Sh} = 1.07 \times 10^{-9} \, . \, N_{Sc}^{0.5} \, . \, N_{Bo}^{1.12} \, . \, N_{Ga}^{1.13} \, . \, N_{Fr}^{0.08} \, . \, (U_l/U_g)^{0.44} \, . \, \varepsilon_g^{1.1} \qquad \ldots (6)$$

where N_{Sh}, N_{Sc}, N_{Bo}, N_{Ga}, and N_{Fr} represent the Sherwood Number ($K_{Li}a_B \, d_c^2 \, / \, D_{H2,l}$), Schmidt Number ($\mu_l \, / \, (\rho_l \, D_{H2,l})$), Bond Number ($d_c^2 \, \rho_l \, g \, / \, \sigma$), Galileo Number ($d_c^3 \, \rho_l^2 \, g \, / \, \mu_l^2$) and the Froude Number ($U_g \, / \, (g \, d_c)^{0.5}$), respectively. The gas phase holdup is best represented by the following expression (Vijayaraghavan, 1994):

$$\varepsilon_g = 0.672 \, . \, (U_g . \mu_l/\sigma)^{0.58} \, . \, (\mu_l^4 \, g/(\rho_l \, \sigma^3)^{-0.13} \, . \, (\rho_g \, /\rho_l)^{0.06} \, . \, (\mu_g \, / \, \mu_l)^{0.11} \qquad \ldots (7)$$

In Equations (6) and (7) d_c, $D_{H2,l}$, μ_l, μ_g, ρ_l, ρ_g, σ, U_l, U_g, ε_g and g represent the column diameter, diffusivity of hydrogen in liquid, viscosity of slurry, viscosity of gas, density of slurry, density of gas, surface tension of oil, velocity of slurry, velocity of gas, gas holdup and gravitational acceleration, respectively.

The development of Equations (2) - (7) used in the computer modeling of the entrained reactor for the liquid phase methanol synthesis process, are described elsewhere (Vijayaraghavan, 1994). The length of the entrained reactor is divided into a number of segments and the concentration of each species in the liquid and vapor phase in each segment is calculated after the physical and chemical equilibrium criteria are met, using computer programs developed earlier (Ko *et al.*, 1987; Lee, 1990). Gas phase holdup, vapor phase compositions, pressure, temperature, volume of oil, and mass of catalyst in each segment of the reactor are required as input data for the next segment in this program. The ratios of reaction of hydrogen, carbon monoxide, carbon dioxide and water with respect to methanol were averaged for the entire data for facilitating modeling purposes. The number of moles of each species entering the (i+1)-th segment of the reactor, is the difference between the number of moles of that species entering the i-th segment and the number of moles of that species reacting in the i-th segment. Thus the number of moles of each reactant and product species entering and exiting each reactor segment is computed cumulatively, and hence the final exiting moles of each species in the reactor is determined.

The data used for the entrained reactor modeling purposes are described elsewhere (Vijayaraghavan, 1994). It is seen from Figure 3 that the experimental data and the modeling results agree well with each other, and the average error between the results is less than 14%. Since hydrogen is no longer the limiting reactant for H_2-rich syngas operating condition, the concentration difference term ($C_{H2} - C^{eq}_{H2}$) plays an important role in the significant deviations observed in Figure 2 for certain experimental runs (5, 11, 16). The average deviation of the computer model seems good considering the extensive thermodynamic computations incorporated in the model, the experimental error, and the wide range of operating conditions employed.

This modeling of the entrained reactor can help to predict the production of methanol for any given inlet conditions and would be extremely useful for the optimization, improvement and scale-up of the methanol synthesis process in a liquid entrained reactor.

CONCLUSION

An overall reaction rate model that could predict the productivity of methanol for any given operating conditions, was successfully developed for the liquid phase methanol synthesis process in an entrained reactor. A computer model that would predict the reactivity of all chemical species involved in the methanol synthesis process in an entrained reactor, from inlet feed conditions was successfully developed. Data covering a wide range of operating conditions, including varying composition of syngas and catalyst loadings, has been used to develop the overall reaction rate model and the computer prediction model. The results obtained could be of great significance in the design, development, scale-up and commercialization of the methanol synthesis process in a liquid entrained reactor.

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Table I

Levels of the Design Variables

Number of the Design Variable	Design Variables	(-)	(+)
1	Temperature (°C)	235	250
2	Pressure (psi)	800	950
3	Syngas Flow Rate (SLPM)	1.0	2.5
4	Slurry Holdup Tank Pressure (psi)	300	500
5	Slurry Flow Rate (l/h)	15	30

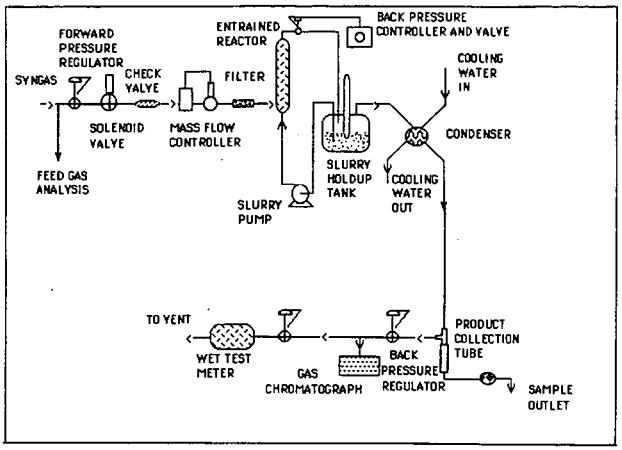

Figure 1. Liquid Entrained Reactor System and its Peripherals

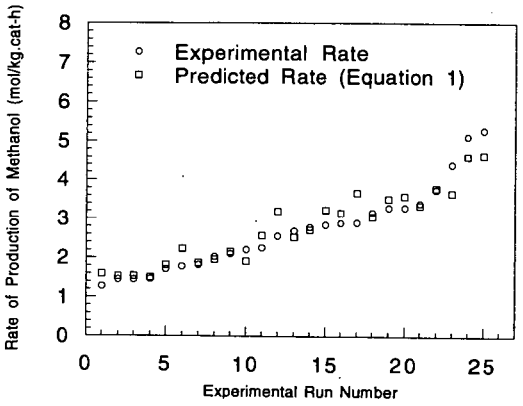

Figure 2. Comparison between Experimental Rate vs. Overall Reaction Rate Model Prediction (Equation 1)

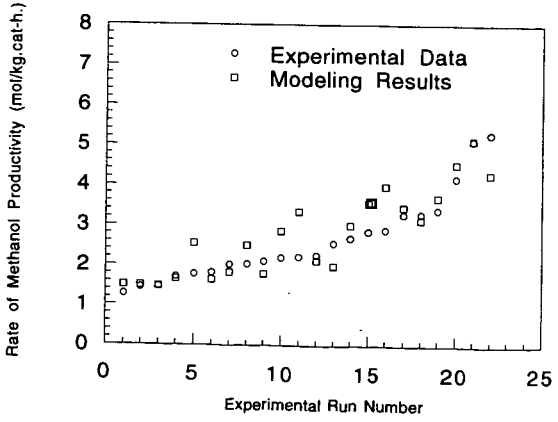

Figure 3. Comparison between Experimental Data vs. Computer Modeling Results